Hollow Nanocrystals Synthesized

Catalytic Properties Measured in Nanoscale Reactors

In a collaboration between the research groups of MSD Scientists Paul Alivisatos and Gabor Somorjai, hollow nanocrystals with a narrow and controlled size distribution have been synthesized for the first time. A simple extension of the process yields metal/metal oxide yolk/shell nanostructures, whose potential catalytic applications as nanoscale reactors were investigated.

Methods for the controlled synthesis of metal nanoparticles have been under investigation since the earliest days of alchemy and the quantitative experiments of Michael Faraday in the mid-19th century. However, despite the great recent success in developing synthetic techniques for nanostructues, including those to make semiconductor core/shell structures (MSD Highlight 99-7) and complex shapes (MSD Highlight 03-9), we have not yet explored the full range of potentially interesting shapes and morphologies. In particular, the synthesis of hollow nanocrystals had not been demonstrated.

The key to achieving hollow nanocrystals lay in a well-known phenomenon in solid-state diffusion. In 1947, Kirkendall described what happens when two solids diffuse into each other at different rates. For example, when two metals, zinc and copper, are place in contact and heated, an alloy (brass in this case) forms at the boundary and expands in the direction of the faster-moving species, zinc. Kirkendall discovered that the atoms of the two solids do not change places directly; rather atoms diffuse into voids in the wake of the faster-moving material. Large pores or cavities form as unfilled voids coalesce.

To exploit this effect on the nanoscale, the Alivisatos groups coat cobalt nanocrystals with sulfur. When exposed to heat, the cobalt atoms rapidly move outward, leaving behind voids, while sulfur atoms move only slowly inward. As a result, a rind of cobalt sulfide forms as they mix while the inner voids coalesce, hollowing out the sphere. Once all the cobalt has diffused outward into the sulfide, an empty sphere of cobalt sulfide remains (see figure). Demonstrating the generality of the technique, the team also made hollow spheres with a number of metals including iron and cadmium and other reactive species including oxygen.

As an initial investigation of a potential application, in collaboration with the Somorjai group, a method was developed to place the catalyst metal, platinum (Pt), inside a hollow sphere. Platinum nanocrystals, which were coated with cobalt to form a core/shell structure, were exposed to oxygen. The outer cobalt shells were oxidized, launching the Kirkendall-like process with the cobalt diffusing rapidly outward and the oxygen slowly inward, forming hollow spheres of cobalt oxide with isolated platinum nanocrystals remaining at their centers. In a test of chemical activity, the confined catalysts efficiently promoted the reaction of ethylene (C_2H_4) and hydrogen to form ethane (C_2H_6), although the mechanism by which the reactants reach the Pt through the shell and the products escape is not fully understood.

The uniformity of the structures and the versatility of the technique suggests a wide range of applications including drug delivery systems, optics, electronics, and selective chemical reactors, all on the nanoscale.

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Yadong Yin, Robert M. Rioux, Can K. Erdonmez, Steven Hughes, Gabor A. Somorjai, and A. Paul Alivisatos, "Formation of hollow nanocrystals through the nanoscale Kirkendall effect," Science 304, 711 (2004).